

SCIENCE FOR GLASS PRODUCTION

UDC 621.315.612.6:666.11(047)

SODIUM-CONDUCTING GLASS FOR ELECTROCHEMICAL EQUIPMENT (Review)

V. L. Mamoshin,¹ N. N. Batalov,¹ G. V. Zelyutin,¹
E. A. Kozyreva,¹ and A. M. Nepomiluev¹

Translated from *Steklo i Keramika*, No. 10, pp. 3–6, October, 1998.

Glass-forming systems with sodium ionic conduction suitable for protecting underground gas pipelines from corrosion are considered.

The high mobility of univalent and bivalent cations in glass, which is a consequence of disordering of the glass structure, makes it possible to consider the glasses with ionic conduction as solid electrolytes (SEL). The advantage of chemical sources of energy (CES) with a separator made of SEL consists in reliable separation of the anode and cathode space, which provides for low currents of CES self-discharge and, consequently, a long service life without deterioration of the service characteristics.

Numerous studies have been performed on the use of SEL in CES which mostly operate at room temperatures. Data on high-temperature CES using SEL with alkali metal ions as conductors are few in number. As a rule, these data refer to rechargeable CES of the Na–S and Na–MeCl_x type with SEL based on β -Al₂O₃. The increased values of the specific conductance of glasses containing cations of alkali metals are of special interest in designing electrochemical cells and batteries of high reliability. In this case, special accent is placed on the alkali elements, since their cations possess high mobility in the disordered lattice of glass.

Satisfactory stability of glasses in time in the case of direct contact with alkali metals maintained up to temperatures of several hundred degrees satisfy another requirement imposed on solid bodies with ionic conduction used as solid electrolytes.

The authors are currently developing an electrochemical sensor capable of monitoring and preventing corrosion of metal gas pipelines which have to operate underground for long periods. In this case, the following requirements are placed on the sensor glass:

electric conduction at temperatures close to room temperature should be at least $10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$;

Na⁺ ions should be charge carriers;

the glass should be resistant to the effect of water, which is required to ensure a long service life for the sensor being developed.

With the view of solving the above problem, among the variety of known glass-forming systems, we selected certain niobium-bearing silicate, phosphate, and borate binary systems as the base, to which sodium oxide was added as the third component. This selection was determined by the ability of niobium oxide to increase the resistance of glass to devitrification.

It is known that silicate glasses with more than 70 mol. % SiO₂ have a three-dimensionally coherent lattice structure, which in binary glasses strongly depends on the nature and content of the second oxide. On introduction of modifiers in SiO₂, the silicon-oxygen lattice gradually depolymerizes, as the level of SiO₂ substitution increases. If the ratio of R₂O: SiO₂ in alkali-silicate glasses increases to 0.5, the degree of coherence of the structural lattice expressed by the ratio between the number of silicon atoms and the number of oxygen atoms decreases to 0.4. It means that in the vertexes of each tetrahedron [SiO₄], one oxygen atom on average is non-bridging, i.e., bond breaks emerge inside the glass skeleton and produce the "voids" in which cations of Na⁺ or other alkali metals can be positioned.

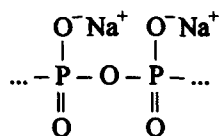
The R⁺ ions arranged statistically in the glass create predominantly ionic bonds and tend to be surrounded with single-bond oxygen atoms and form [RO_n] polyhedrons. At the same time, with an increase in the content of RO₂ oxides in the glass, the number of non-bridging oxygen atoms surrounding the R⁺ ions increases, which causes concealed

¹ Ural State Technical University (UGTU–UPI), Ekaterinburg, Russia; Institute of High-Temperature Electrochemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia.

stratification, i.e., isolation of microregions enriched with these cations, and the coordination requirements of R^+ ions are more easily satisfied within these microregions than in the case of uniform distribution of R^+ ions. In this way, chemical inhomogeneity of the glass is formed.

The effect produced by addition of other glass-forming oxides or conventional glass-formers, such as Nb_2O_5 to silica perceptibly differs from the effect of introduction of modifiers. The former and the latter can structurally replace silicon oxide by being incorporated into the silicon-oxygen skeleton and contributing to preservation of the three-dimensional glass lattice.

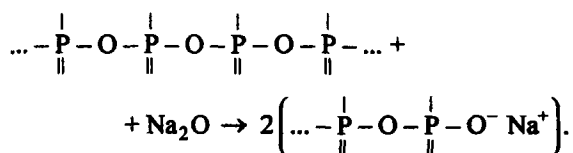
The specific properties of phosphate glasses are largely determined by the peculiarities of their polymer-chain structure. According to the data in [1], phosphate glasses, like silicate glasses, form continuous structural skeletons consisting of interrelated $[PO_4]$ tetrahedrons. They are the closest analogues of linear organic polymers [2]. Unlike silicate glasses, which are typical three-dimensional polymers, phosphate glasses are characterized by the presence of chains with a weak Van-der-Vaals effect between them, although the structure of vitreous P_2O_5 can be branched as well [3]. The main structure-forming unit of phosphate glasses is the $[PO_4]$ tetrahedron which has one unshared electron pair in the phosphorus-oxygen bond:



This peculiarity of the phosphorus-oxygen tetrahedron is responsible for the low melting point of P_2O_5 and low softening temperature of phosphate glasses.

Compared to the silicon-oxygen tetrahedron, the $[PO_4]$ group is not geometrically correct. The $P=O$ double bond is not capable of extending the glass lattice, since both valence bonds of the oxygen are satisfied. Moreover, this bond is shorter than the rest of the $P-O$ bonds. Therefore, the $(PO_3)_n$ metaphosphate chains consist of distorted $[PO_4]$ tetrahedrons so that the structure of phosphate glass is less strong and more mobile than the silicate glass structure.

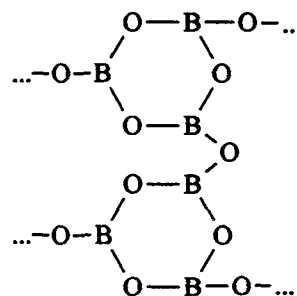
Introduction of modifying oxides, e.g., Na_2O , has a depolymerizing effect on the phosphorus-oxygen bonds according to the following mechanism:



Based on the assumption that vitreous phosphoric anhydride consists of chains of the sillimanite type, a scheme for

depolymerization of the phosphorus-oxygen skeleton by introducing oxides of alkali metals in the composition of vitreous P_2O_5 was suggested in [4]. According to this scheme, the $(P_2O_5)_\infty$ chain is gradually transformed into a chain of $(3P_2O_5 - R_2O)_\infty$ composition and ends with a chain of metaphosphate $(P_2O_5 - R_2O)_\infty$. A further decrease in the degree of polymerization results in splitting of the metaphosphate chains into smaller fragments.

The structure of vitreous boron oxide was repeatedly investigated by diffraction and spectroscopic methods. The obtained results revealed that the main structural unit of vitreous B_2O_3 is a boroxol group, which is a flat hexagonal ring formed by atoms of boron and oxygen. These groups are joined in a three-dimensional lattice by bridging oxygen atoms:



The structure of borate glass in which boron is predominantly in three coordination is formed by layers consisting of $[BO_3]$ groups with a weak Van-der-Vaals interaction between the layers. Such glass is extremely low-melting.

Introduction of alkali metal oxides in B_2O_3 produces results which are distinct from silicate glasses. The borate glass exhibits what is known as the boron anomaly. The study of borate glass using the nuclear magnetic resonance method on ^{11}B nuclei revealed that addition of R_2O to B_2O_3 results in variation of the coordination number of boron from 3 to 4 ($B^{III} \rightarrow B^{IV}$ transition). When the ratio of $Na_2O : B_2O_3$ reaches 0.5, nearly 50% of the boron atoms are arranged in four (tetrahedral) coordination, regardless of which particular alkali metal oxide is used. A determining role in the $B^{III} \rightarrow B^{IV}$ coordination transition belongs to the "excess" oxygen atoms introduced in the glass-forming lattice together with R_2O . The introduced oxygen forms bridges which cross-link the above mentioned layers consisting of boroxol rings. The rigidity of the borate glass skeleton thus increases.

The behavior of niobium in glasses of different nature is sufficiently well investigated [5-7]. Some researchers believe that the structural role of niobium in alkaline-silicate glasses depends on the concentration of Nb_2O_5 in the composition of glass. With a low molecular content of this oxide, niobium strengthens the glass structure, and with 15-20% of Nb_2O_5 , its structural role is changed, which disturbs the linear dependence between the composition and properties. Introduction of niobium oxide in silicate glass in quantities

exceeding 20% produces depolymerization of the silicon-oxygen skeleton.

In phosphate glasses, the niobium ion can likewise play a double role [5]: as a lattice-former in the composition of $[\text{NbO}_4]$ groups and as a modifier in $[\text{NbO}_6]$ polyhedrons. In this case, its significant effect on the physicochemical properties is observed until the molar content of Nb_2O_5 reaches 10–15%, and above that content, the properties change insignificantly [6]. The inflections on the composition-property curves in the specified concentration region are evidence of structural modifications in the glass caused by partial transition of Nb^{5+} ions from four coordination to six coordination by oxygen.

Being in six coordination, i.e., acting as a modifier, niobium can have a strengthening effect on the structure of the phosphorus-oxygen skeleton of phosphate glass owing to stabilization of P–O–P valence bond angles [7]. This stabilization ensues from an increase in the coordination number of the bridging oxygen atoms, though on the other hand, the niobium in the composition of the $[\text{NbO}_6]$ octahedrons can be incorporated in the phosphate glass lattice acting as a lattice-former.

Passing to six coordination, the niobium atoms borrow oxygen from the $[\text{PO}_4]$ tetrahedrons, since there are only 2.5 oxygen atoms per one niobium atom in Nb_2O_5 , and three oxygen atoms per one atom of niobium in $[\text{NbO}_6]$ octahedrons. By generalizing the bridging oxygen atoms of the neighbour chains of –P–O–P–, niobium has a strengthening effect on the structure of vitreous polyphosphates. As a result of cross-linking of the phosphorus-oxygen chains by the $[\text{NbO}_6]$ polyhedrons, the rigidity of the phosphate glass skeleton increases.

It is obvious that the organization of the structural groups is in direct dependence on the concentration of the non-bridging oxygen atoms of –P–O–P– chains. With a certain content of Nb_2O_5 in the composition of glass, there is a shortage of the mentioned atoms, therefore part of the Nb^{5+} ions has to be surrounded both by bridging and nonbridging oxygen atoms, i.e., the structural role of the niobium changes.

Electric conduction in solid bodies is implemented by migration of electrons and ions. Most often, conduction determined by only one of these types of charge carriers is predominant. However, in some inorganic materials, both ionic and electronic conduction can exist simultaneously. The specific conductivity of any material, regardless of the type of charge carrier, is determined by the equation:

$$\sigma = \sum_i n_i e_i \mu_i,$$

where n_i is the number of the current carriers; e_i and μ_i are their charge and mobility, respectively; for electrons and singly-charged ions $e = 1.6 \times 10^{-19}$ C (the electron charge).

A large group of oxide glasses, including silicate, phosphate, and borate glasses, belongs to the class of insulators, which is determined by the large values of the forbidden

band width. The electric conduction of these glasses at room temperature amounts to $10^{-8} - 10^{-19} \Omega^{-1} \cdot \text{cm}^{-1}$. At the same time, some glasses have high conductivity. They primarily include alkali-rich glasses, whose conductance in the range from the softening temperature to room temperature is determined by R^+ ions [8].

The experiments show that not all current-carrying ions migrate with simultaneous ease. There are only a few kinds of ions which significantly contribute to electric conduction at room temperature. This group includes Li^+ , Na^+ , and K^+ ions. The sizes of the lithium and sodium ions are relatively small. They have a low charge and therefore can easily migrate in the glass lattice. They are known as mobile ions [9].

Ionic conduction in crystalline solid bodies is probably characterized by the "jump" mechanism, when the ions overcome energy barriers of the same height. Apparently, in glass there are potential barriers of different heights due to the disordered structure of the material and the fact that not all positions in glass are equivalent. Thus, Na^+ ions in migration have to overcome potential barriers that can be either high or low. Ion transfer in glasses can be attributed to the fact that there is a potential field around each alkaline cation. Such a model allows for two types of ionic transitions.

The first type consists in turning of the O – Cat dipole by jumping of the cation (Cat) from one position to another around the nonbridging oxygen (O). This adds to the dielectric losses, and yet does not result in progressive movement of the ions in a constant electric field.

The second type of ion migration proceeds in two phases. First, a cation leaves its position near the non-bridging oxygen. As a result, a pair of "defects" emerges: the first nonbridging oxygen atom does not have a single cation in its immediate vicinity, and the second one has two cations. Further migration of cations can be ensured either by filling of the vacancy near the first nonbridging oxygen by transitions of the neighboring cations, or by jumps of the "excess" cation from the second nonbridging oxygen via allowed positions. In this scheme, the anomaly involving transfer of current by crystal defects according to Frenkel is clearly observed. The excessive cations near the non-bridging oxygen here act as interstitial cations. The first phase of the mechanism described above is related to the formation of defects, and the second phase is due to their migration.

Solid electrolytes include various classes of substances possessing a common property: the determining role of ion migration in the transfer processes, in particular, predominance of ionic conduction of electric current. The definition suggested in [10] defines solid electrolytes as materials whose ionic conduction is sufficiently high: $> 10^{-10} \Omega^{-1}$.

At the same time, substances with significantly different structures are attributed to solid electrolytes: ionic crystals, covalent bond crystals, mixed bond crystals, glasses. The interest in solid electrolytes is currently growing, due to miniaturization technologies which require small-scale current sources.

Owing to the fact that glasses are isotropic, the indeterminacy typical of polycrystalline solids and related to the existence of grain boundaries is not present in glasses. Ionic conduction in vitreous materials can be optimized by two methods. First, the mobility of cations can be increased by means of conversion from oxide systems to chalcogenides. Second, the structure of oxide glasses can be loosened by introduction of salts with relatively large cations in glass compositions [11].

In spite of the existence of numerous theories explaining the origin of high ionic conduction, it is currently hard to predict the reasons for the increase in ionic conduction, although the basic prerequisites are as follows [10]:

the presence of a large amount of mobile ions of the same type in the glass;

the presence of a large number of vacant positions accessible to mobile ions;

a slight difference in the energy of occupied and vacant positions, and a low value of the activation barrier taken by an ion which jumps from one position to another;

the presence of open channels for migration of mobile ions in the glass structure;

the anionic sublattice of glass has to be easily polarized.

REFERENCES

1. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1974).
2. Van Vazer, *Phosphorus and Its Compounds* [in Russian], Nauka, Moscow (1962).
3. V. V. Tarasov, *New Problems of the Physics of Glass* [in Russian], Gosstroizdat, Moscow (1959).
4. A. V. Gladkov, "Vitreous systems and new materials based on glass," *Stekloobr. Sost.*, 3(4), (1964).
5. N. M. Bobkova and G. E. Rachkovskaya, "The structural role of niobium in glasses," *Fiz. Khim. Stekla*, 2(3), 23 – 27 (1976).
6. N. M. Bobkova and G. E. Rachkovskaya, "New low-melting glazes, enamels, and phosphorus-bearing glasses," in: *Proc. of Republ. Conf.* [in Russian], Riga (1973).
7. A. P. Shtin, A. D. Galaktionov, V. V. Makarov, and V. L. Mamoshin, "On the structural role of niobium in glasses of the $K_2O - Al_2O_3 - P_2O_5 - Nb_2O_5$ system," *Fiz. Khim. Stekla*, 3(3), 201 – 208 (1977).
8. O. V. Mazurin, *Electrical Properties of Glass* [in Russian], Nauka, Leningrad (1962).
9. J. Stevels, *Electrical Properties of Glass* [Russian translation], Mir, Moscow (1982).
10. A. Vest, *Chemistry of Solids* [Russian translation], Mir, Moscow (1988).
11. A. Feltz, *Amorphous and Vitreous Inorganic Solids* [Russian translation], Mir, Moscow (1986).